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SEPTEMBER, 1941

NUMBER 9

RESONANCE METHOD OF MEASURING THE RATIO OF THE SPECIFIC HEATS OF A GAS, C_p/C_v . PART III.¹

SULPHUR DIOXIDE AND NITROUS OXIDE

By A. L. CLARK² AND L. KATZ³

Abstract

This paper is a continuation of work published in the Canadian Journal of Research in 1940. The results for nitrous oxide and sulphur dioxide are now shown. A paper now in preparation will deal with some theoretical matters and will contain additional results for some of the gases already discussed.

In previously published papers (3) the authors developed the theory of a resonance method for measuring the ratio of the specific heats of gases, γ , and gave the results for a number of the gases at pressures up to 25 atm. at room temperature.

The resonance method is particularly suitable for measuring the variation of γ with pressure at constant temperature. Such measurements were carried out on helium, argon, nitrogen, hydrogen, and carbon dioxide. The values of γ at zero pressure were found by extrapolation and were listed in Table XV of Part II. Later examination showed these values to agree with those calculated from spectroscopic data to better than 0.1% with the exception of the value for carbon dioxide which was found to be 0.49% too large. Since this was the only triatomic gas investigated at that time, it was felt advisable to examine other triatomic gases. With this purpose in mind sulphur dioxide and nitrous oxide were investigated.

Sulphur Dioxide

This gas was obtained from the Ohio Chemical Company who gave its purity as better than 99.5%. For this reason the gas was used without any further purification.

To calculate the correction factors G and Λ it was necessary to have experimental $Pv - P$ data or an equation of state capable of yielding the derivative $(\partial v/\partial P)_T$ with a fair degree of accuracy. There are surprisingly few pressure-volume data on sulphur dioxide to be found in the literature. One paper,

¹ Manuscript received July 3, 1941.

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by W. Cawood and H. S. Patterson (2) lists the first virial coefficient as a function of temperature for a number of gases, that is, values of A in the empirical equation,

$$Pv = RT(1 - Ap), \quad (1)$$

from which

$$G = -P/v \cdot (\partial v / \partial p)_T = 1 + \frac{ART}{v} = \frac{1}{1 - AP}. \quad (2)$$

In the case of sulphur dioxide, we find $A = 0.0173$ at 25.1°C . The correction factor Λ is given by the equation

$$\Lambda = \frac{m + m_g}{m} = \left(1 + \frac{104.02}{143.69v}\right), \quad (3)$$

where v is the specific volume of the gas in cubic centimetres per gram, obtained from Equation (1).

For comparison we may use Wohl's equation of state, which seems to be suitable for this gas over a wide range of temperatures and pressures with a fair degree of accuracy (6). This equation may be written in the form

$$P = \frac{RT}{v - b} - \frac{a}{Tv(v - b)} + \frac{c}{T^{4.2}v^3}, \quad (4)$$

with

$$a = \frac{32}{75} \cdot \frac{R^2 T_k^2}{p_k}, \quad b = \frac{RT_k}{15p_k}, \quad c = 0.07585 \frac{R^2 T_k^{13/3}}{p_k^2},$$

where T_k = critical temperature, p_k = critical pressure. The equation for G follows directly, and is

$$\frac{1}{G} = 1 + \left(RTb - \frac{a}{T} \right) \frac{1}{P(v - b)^2} + \frac{2c}{PT^{4.2}v^3} \quad (5)$$

For sulphur dioxide at 25.1°C ., this reduces to

$$\frac{1}{G} = 1 - \frac{2299.8}{P(v - b)^2} + \frac{7077.5}{Pv^3}, \quad (6)$$

with

$$P = \left(394.83 - \frac{2486.4}{v} \right) \frac{1}{v - b} + \frac{3538.8}{v^3}. \quad (7)$$

As before, the factor Λ is calculated by means of Equation (3) with v obtained from Equation (6).

Table I gives the corresponding resonance frequencies and correction factors for sulphur dioxide at various pressures. The factors Λ and G were calculated from the data of Cawood and Patterson. In Part II a quantity $\Delta\gamma$ was added to γ to correct for the fact that the compressions are not strictly adiabatic. The equation for $\Delta\gamma$ was derived by an approximation method. A more accurate analysis gives a correction factor that may be expressed in terms of $\Delta\gamma$ as

$$\Gamma = 1 + 0.83 \frac{\Delta\gamma}{\sqrt{\gamma}} + 0.69 \frac{(\Delta\gamma)^2}{\gamma}$$

The complete derivation of Γ and its effect on previously published values will be given in Part IV of this series of articles. In the meantime it is used in the present calculations and values of Γ are listed in Table I. The final corrected values of γ are listed in Column 6. A second degree curve was fitted to these values by the method of least squares and was found to be

$$\gamma = 1.2642 + 0.0169P + 0.0026P^2. \quad (8)$$

TABLE I
SULPHUR DIOXIDE (25.1° C.)

Press., atm.	Frequency at resonance	Λ	G	Γ	γ	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}}) \times 10^{-3}$
0.9970	26 032	1.00192	1.0175	1.0039	1.283 ₂	1.2836	-0.3
2.241	29 070	1.00440	1.0403	1.0022	1.315 ₂	1.3152	0
2.8705	44 269	1.00570	1.0523	1.0020	1.335 ₂	1.3341	+1
3.641	49 914	1.00733	1.0670	1.0018	1.359 ₂	1.3602	-1

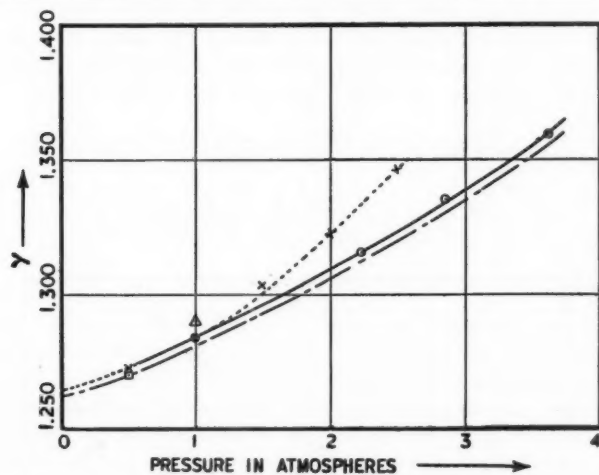


FIG. 1. Sulphur dioxide— γ as a function of pressure at 25.1° C. $\gamma = 1.2642 + 0.0169P + 0.00260P^2$. — Curve using Carwood and Patterson $Pv - P$ data to calculate Λ and G . - - - Using Wohl equation of state to calculate Λ and G . \circ , Clark and Katz. \times , Scholer (20° C.). \square , Capstick. Δ , I.C.T. (15° C.) also Partington and Cant (20° C.).

Values of γ calculated from Equation (8) are given in Column 7 and are compared with the corrected values in Column 8. Both are plotted in Fig. 1. If the Wohl equation is used, the correction factors are altered sufficiently to lower all the values of γ by about 0.2% as shown by the broken-line curve in Fig. 1. The equation for this curve by the method of least squares is

$$\gamma = 1.2620 + 0.0165P + 0.00265P^2.$$

The authors feel that the results obtained by use of the data of Cawood and Patterson are the more reliable. The friction factor χ was found to be very close to unity ($\chi < 1.00002$) and was neglected.

A few experimental values found in the literature are also shown in Fig. 1. The values of Scholer (5) were given at 20° C. and are plotted without change. They would be altered only slightly (about 0.2% in the lower pressure range) when corrected to 25.1° C. His values for pressures of $\frac{1}{2}$ and 1 atm. are in good agreement with those of the authors, but those at the higher pressures are larger. A single value by Capstick (1) at $\frac{1}{2}$ atm. pressure and another by Partington (4) at 1 atm. and 20° C. are also shown.

Nitrous Oxide

This gas was obtained from the same company as the sulphur dioxide and its purity was given as 98%. As in the case of sulphur dioxide, the only $Pv - P$ data found in the literature for calculating the correction factors were those of Cawood and Patterson (2), and even these are given only for pressures up to 5 atm. For higher pressures the Wohl equation was again used, and it was reassuring to note that within the common pressure range up to 5 atm. the values of γ calculated by the two methods agreed to within less than 0.1%. For nitrous oxide at 25.1° C. the Wohl equation reduces to

$$P = \left(538.85 - \frac{1933.6}{v} \right) \frac{1}{(v-b)} + \frac{2515.1}{v^3}, \quad (9)$$

giving

$$\frac{1}{G} = 1 - \frac{1635.8}{P(v-b)^2} + \frac{5030.2}{Pv^3}. \quad (10)$$

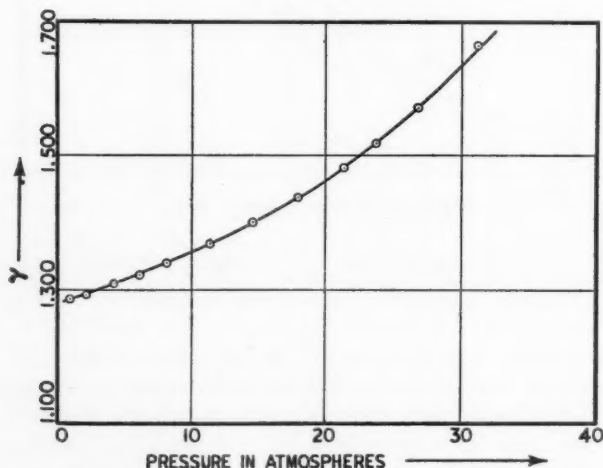


FIG. 2. Nitrous oxide— γ as a function of pressure at 25.1° C. $\gamma = 1.2783 + 6.320 \times 10^{-3} P + 1.22 \times 10^{-4} P^2 + 6.80 \times 10^{-8} P^4$.

As before, Λ is calculated from Equation (3) with the values of ν for particular pressures given by Equation (10).

Table II summarizes the authors' work on this gas. A fourth degree curve fitted to the corrected values of γ as listed in Column 6 was found to be

$$\gamma = 1.2783 + 6.320 \times 10^{-3}P + 1.22 \times 10^{-4}P^2 + 6.80 \times 10^{-8}P^4. \quad (11)$$

Values of γ calculated from this equation are given in Column 7 and are compared to the corrected values in Column 8. The corrected values are plotted as a function of the pressure in Fig. 2. The full line drawn through these values is given by the Least Square Equation (11).

TABLE II
NITROUS OXIDE (25.1° C.)

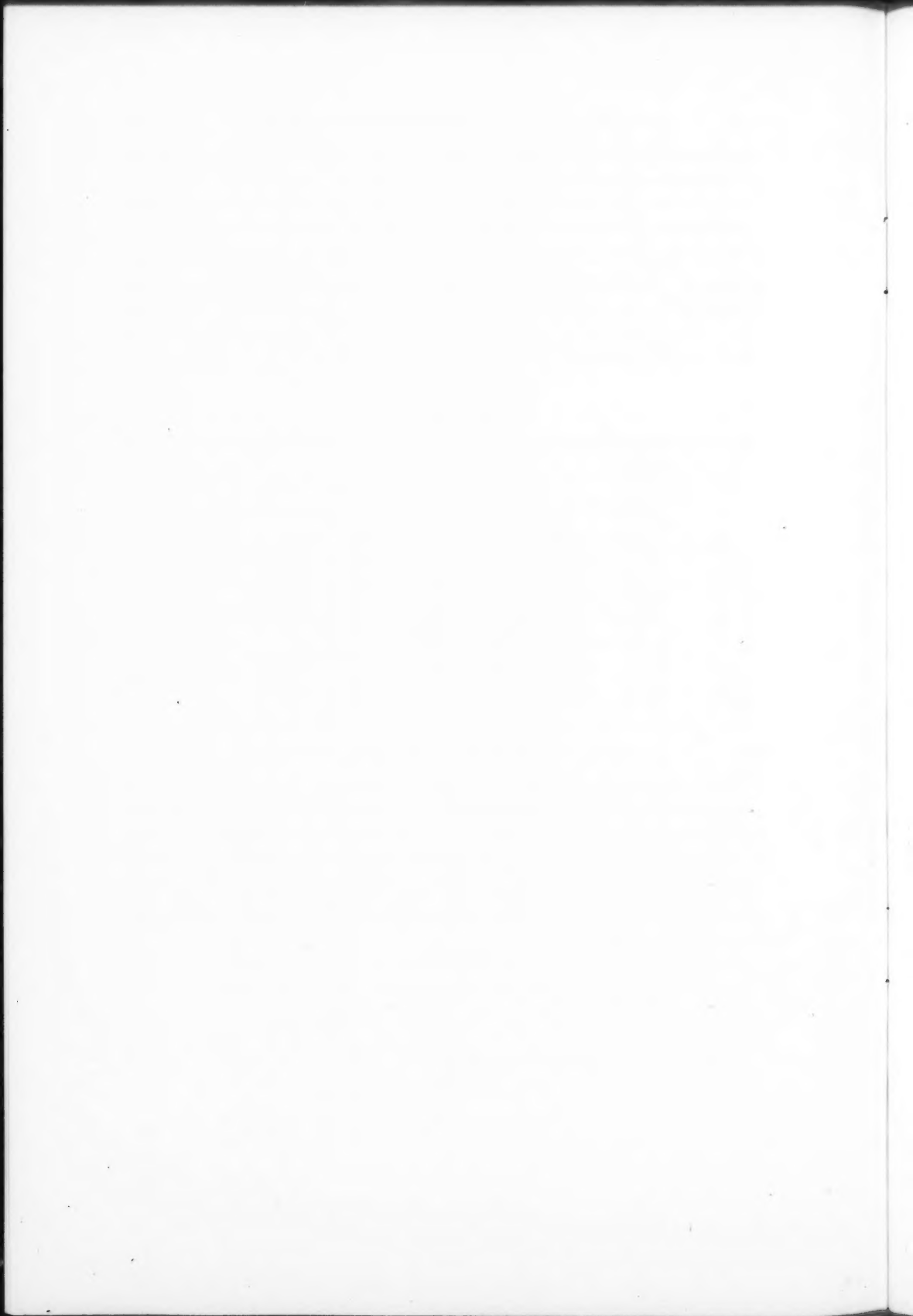
Press., atm.	Frequency at resonance	Λ	G	Γ	γ	$\gamma_{\text{calc.}}$	$(\gamma - \gamma_{\text{calc.}}) \times 10^{-4}$
0.9987	26.211	1.00135	1.0057	1.0054	1.2847	1.2847	0
2.224	39.106	1.00303	1.0129	1.0031	1.292	1.2930	-1
4.334	51.568	1.00597	1.0259	1.0019	1.308	1.3080	0
6.157	64.870	1.00858	1.0379	1.0015	1.322	1.3220	0
8.208	74.782	1.01158	1.0519	1.0013	1.339	1.3407	-2
11.439	88.030	1.01648	1.0754	1.0011	1.368	1.3678	0
14.641	99.206	1.02169	1.1043	1.0010	1.400	1.4001	0
17.952	109.560	1.02707	1.1341	1.0009	1.438	1.4382	0
21.384	119.156	1.03312	1.1710	1.0009	1.483	1.4836	-1
23.769	125.304	1.03756	1.2001	1.0008	1.519	1.5189	0
26.942	133.008	1.04376	1.2441	1.0008	1.574	1.5731	+1
31.354	142.645	1.05315	1.3193	1.0008	1.664	1.6621	+2

Analysis of Results

Since the equations fitted to the experimental data give equal weight to all the measurements made on each gas, it is felt that the values given by these equations are relatively free of accidental errors, and are more accurate than the experimental values themselves. These results will be analysed in Part IV of these articles, which the authors hope to publish at an early date. It will be shown that the zero pressure value of γ for sulphur dioxide agrees perfectly with that calculated spectroscopically but that the nitrous oxide value is 0.38% too large.

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THE OXIDATION OF PYROLYTIC DISTYRENE¹

BY LÉO MARION²

Abstract

The pyrolysis of polystyrene to distyrene is accompanied by the formation of 1,3,5-triphenylbenzene. When pyrolytic distyrene is oxidized with limited quantities of potassium permanganate, a mixture of β -phenylpropiophenone, benzoic acid, and α -hydroxy- α,γ -diphenylbutyric acid is obtained. This substituted butyric acid can further be oxidized to β -phenylpropiophenone, and when it is treated with hydrogen bromide and subsequently with sodium amalgam it gives rise to α,γ -diphenylbutyrolactone. The relation of these results to the structure of the ethylenic component of pyrolytic distyrene is discussed.

It is well known that when highly polymerized styrene is distilled *in vacuo* it is pyrolysed and yields a mixture of products from which one fraction can be separated which is generally termed distyrene. This fraction has been shown by Staudinger and Steinhofer (6) to consist of a mixture of α,γ -diphenylpropane and an unsaturated component that had been assumed by various authors to possess the structure of 1,3-diphenyl-3-butene (I).



Staudinger and Steinhofer (6) were the first to attempt to support such a structure with chemical evidence. Having obtained β -phenylpropiophenone as a product of the oxidation of pyrolytic distyrene they considered structure I for the unsaturated component as established. It has been shown since (4), however, that α,γ -diphenylpropane, when oxidized, produces an excellent yield of β -phenylpropiophenone, so that the proof of the structure of the unsaturated component of pyrolytic distyrene no longer holds. In an attempt to elucidate the structure of this unsaturated substance a study of its oxidation products has been undertaken.

Polystyrene was pyrolysed and the product fractionated into styrene, distyrene, the so-called tristyrene, and a crystalline product identified as 1,3,5-triphenylbenzene. This confirms the observation of Staudinger and Steinhofer (6) who have already recorded the formation of 1,3,5-triphenylbenzene under the same conditions. It has now further been found that if the tristyrene fraction is redistilled under atmospheric pressure, it is cracked into styrene and distyrene, and the process is accompanied by the formation of an appreciable quantity of 1,3,5-triphenylbenzene.

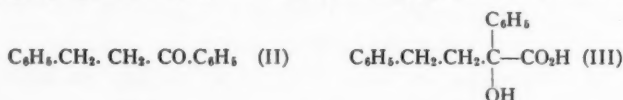
¹ Manuscript received July 17, 1941.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1008.

² Chemist.

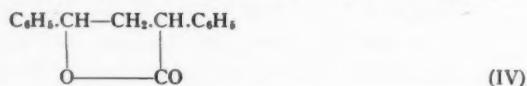
Treatment of distyrene with nitrogen tetroxide yielded intractable gums which, after nitration and oxidation, produced *p*-nitrobenzoic acid. The nitration of distyrene with fuming nitric acid failed to yield the expected tetranitro-diphenylpropane but gave rise to a small quantity of *p*-nitrobenzoic acid. The failure to isolate the tetranitro derivative of diphenylpropane may be due to the presence of the other component of distyrene, which might prevent it from crystallizing. However, the readiness with which *p*-nitrobenzoic acid was obtained in these experiments harmonizes with the fact that all attempts to oxidize distyrene yielded benzoic acid as one of the products.

In the course of numerous experiments to oxidize pyrolytic distyrene in acetone solution with limited amounts of potassium permanganate, it was observed that the β -phenylpropiophenone produced was always accompanied by an appreciable quantity of an acid resembling benzoic acid. Repeated recrystallization, however, could not bring the melting point above 113 to 116° C. The acid was, therefore, esterified and the product fractionated into ethyl benzoate and an ester of higher boiling point. The latter, when saponified, gave rise to a crystalline acid yielding analytical figures in good agreement with $C_{16}H_{16}O_3$. The acid could not be distilled without decomposition, a characteristic of α -hydroxy acids. Furthermore, when the acid was oxidized with potassium permanganate, it gave an excellent yield of β -phenylpropiophenone (II). In view of the analytical results this characterizes



the acid as an α,γ -diphenylhydroxybutyric acid. Substituted α -hydroxy-acids can be oxidized to carbonyl compounds, as exemplified by α -hydroxyisobutyric and benzilic acids, which yield acetone and benzophenone respectively (2). Hence, the oxidation of the styrene degradation acid to β -phenylpropiophenone is a further and more definite indication that its hydroxyl group is attached to the α -position. The acid, therefore, must be α -hydroxy- α,γ -diphenylbutyric acid (III) and is an intermediate product in the oxidation of distyrene to β -phenylpropiophenone.

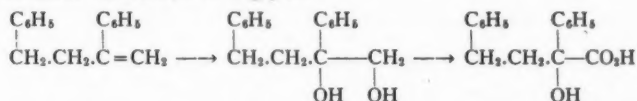
It was thought that were such an acid to be treated with hydrogen bromide and the resulting bromo acid reduced with sodium amalgam, the final product should be α,γ -diphenylbutyric acid. When these reactions were carried out, however, α,γ -diphenylbutyrolactone (IV) was produced. The rearrangement



necessary to produce this lactone may have taken place in alkaline solution in the intermediate unsaturated acid formed after hydrogen bromide had been removed from the molecule. It is well known that α,β double bonds

of this type shift to the β,γ -position in the presence of alkali (3). In this case the β,γ double bond, being conjugated, would have no tendency to shift back to its original position. The elements of water would then be added at the double bond and the lactone formed, during the subsequent treatment of the acid. Whatever the mechanism of its formation, the production of α,γ -diphenylbutyrolactone is an additional proof that the oxidation acid is an α,γ -diphenylhydroxybutyric acid.

The mechanism of the formation of α -hydroxy- α,γ -diphenylbutyric acid from 1,3-diphenyl-3-butene (I) may be postulated as taking place through the intermediate formation of a glycol:



It would not be possible, on the other hand, to obtain such a hydroxy-acid from the oxidation of any of the other isomeric forms of 1,3-diphenylbutene unless the oxidation were preceded by a rearrangement into 1,3-diphenyl-3-butene. It has been shown (4) that 1,3-diphenyl-3-butene is unstable and that it isomerizes on standing. If this hydrocarbon be assumed to be the ethylenic constituent of pyrolytic distyrene then the latter must consist of a mixture of α,γ -diphenylpropane, 1,3-diphenyl-3-butene, and one or more of its isomeric forms. Among its products of oxidation, one of these isomeric forms (i.e., 1,3-diphenyl-1-butene) should produce benzoic acid, while the other (i.e., 1,3-diphenyl-2-butene) should produce phenylacetic acid. Hence, the fact that α -hydroxy- α,γ -diphenylbutyric acid is always accompanied by an almost equal quantity of benzoic acid seems to support this assumption concerning the components of pyrolytic distyrene.

Experimental

Oxidation of Distyrene to *p*-Nitrobenzoic Acid

The gases produced by heating lead nitrate (40 gm.) were absorbed in hexane (100 cc.) cooled in an ice-salt mixture, and the solution was added to a chilled solution of distyrene (6.5 gm.) in hexane (100 cc.). The product gradually separated as an oil at the bottom of the flask. As nothing could be induced to crystallize from this oil it was treated in the cold with fuming nitric acid but, this failing again to give crystals, the product was oxidized in acetone solution with potassium permanganate. An acid was thus obtained which, after several recrystallizations from ethyl acetate, melted at 241° C.* In admixture with an authentic specimen of *p*-nitrobenzoic acid (m.p. 242°) it melted at 241°. Calc. for $\text{C}_7\text{H}_5\text{O}_4\text{N}$: C, 50.29; H, 2.99; N, 8.38%. Found: C, 50.88, 50.74; H, 3.35, 3.22; N, 8.25, 8.19%.

When distyrene was treated with fuming nitric acid, it also yielded a small quantity of *p*-nitrobenzoic acid accompanying the bulk of neutral, uncrystallizable product.

*All melting points are corrected.

Pyrolysis of Polystyrene

Styrene was heated in a sealed tube at 170° C. for 72 hr. and the resulting polymer dissolved in benzene and fractionally precipitated with methanol. The fraction of average molecular weight 8000 was pyrolysed *in vacuo* according to the usual procedure (6). A total crude distillate weighing 979 gm. was obtained from 1150 gm. of polymer, representing a yield of 88.2%. The crude product was fractionated under diminished pressure. It yielded styrene, b.p. 28 to 34° (5 mm.), wt. 403 gm.; distyrene, b.p. 135 to 180° (3.5 mm.), wt. 161.5 gm.; and the so-called tristyrene, wt. 390.7 gm. Towards the end of the distillation, the temperature rose to 360 to 400° and a substance distilled over which crystallized in the receiver.

The tristyrene fraction was cracked, by distilling slowly under atmospheric pressure. It yielded styrene (188 gm.), distyrene (52.2 gm.), and finally a thick oil, which was dissolved in methanol and allowed to stand. This solution gradually deposited the same solid that was obtained in the pyrolysis *in vacuo* of the more highly polymerized styrene.

The combined crude distyrene fractions (213.7 gm.) were refractionated and the main cut, b.p. 140 to 145° C. (3 mm.) was collected. Wt. 186.4 gm. (17% of the polystyrene used).

Isolation of 1,3,5-Triphenylbenzene

The solid obtained in the pyrolysis of polystyrene and in the cracking of tristyrene was recrystallized from boiling methanol from which it separated as flat needles. It was sublimed *in vacuo*, 185° C. (0.5 mm.), and recrystallized repeatedly from alcohol. It was finally obtained as small colourless prisms, m.p. 176°. Wt. 7.5 gm. Calc. for $C_{24}H_{18}$: C, 94.12; H, 5.88%. Found: C, 94.43; H, 5.64%.

When this hydrocarbon was oxidized with chromic-acid-acetic-acid it yielded some unchanged hydrocarbon and an acid found to be benzoic acid; m.p. 124° C., either alone or in admixture with an authentic specimen.

1,3,5-Triphenylbenzene was synthesized from acetophenone, potassium pyrosulphate, and sulphuric acid by the method of Odell and Hines (5). The product, after several recrystallizations from benzene-methanol, melted at 176° C., either alone or in admixture with the pyrolytic solid hydrocarbon.

Oxidation of Pyrolytic Distyrene

Distyrene (50 gm.) was dissolved in acetone previously distilled over potassium permanganate, dried with calcium chloride, and redistilled (500 cc.). Finely ground potassium permanganate in portions each equivalent to one-quarter atom of oxygen (6.33 gm.) was added to the solution kept cool with running water. The total potassium permanganate added was equivalent to 3.5 atoms of oxygen. The manganese dioxide sludge was then filtered out and washed with acetone. The combined filtrate and washings were distilled on the steam-bath, the oily residue was dissolved in ether, washed repeatedly with dilute sodium hydroxide, and with water. After drying over

sodium chloride, the ether was distilled off and the oily residue allowed to cool. It crystallized immediately to a solid mass, wt. 38.3 gm. This was recrystallized from petroleum ether, from which it separated as flakes, m.p. 72° C. Admixture with β -phenylpropiophenone failed to depress the melting point. Some of the oxidation ketone was converted to the oxime which was recrystallized once from aqueous methanol and several times from petroleum ether; m.p. 83°, either alone or in admixture with an authentic specimen of β -phenylpropiophenoneoxime.

Isolation of Benzoic and α -Hydroxy- α,γ -diphenylbutyric Acids

The manganese dioxide sludge, which had been filtered, was suspended in water and a stream of sulphur dioxide passed through the suspension until all the manganese dioxide had dissolved. The acid that precipitated was collected in ether and the solution washed thoroughly with water, dried over sodium chloride, and distilled on the steam-bath. From 186 gm. of distyrene, 71.4 gm. of crude acid was obtained.

The crude acids were dissolved in dilute sodium hydroxide and the solution was extracted with ether, acidified with hydrochloric acid, and again extracted with ether. The second ether extract was washed with water, dried over sodium chloride, and distilled on the steam-bath. Wt. of crystalline acid, 46.7 gm. This was dissolved in absolute ethyl alcohol (235 cc.) containing concentrated sulphuric acid (23.5 gm.) and the solution refluxed for five hours on the steam-bath. About two-thirds of the alcohol was then distilled off and the residual oil poured into cold water (one litre). The precipitated oil was collected in ether, washed with water, with dilute sodium hydroxide, and again with water. It was dried over sodium chloride and distilled on the steam-bath. The residual ester (45.4 gm.) was distilled *in vacuo* through a fractionating column. Two fractions were collected: (a) b.p. 95° C. (6 mm.), wt. 17 gm., and (b) b.p. 195 to 200° (6 mm.), wt. 22.1 gm. The latter weight represents a yield of 9.6% calculated on the weight of distyrene used. The second fraction was redistilled and the cut, b.p. 184 to 187° C. (4 mm.), collected. Wt., 19.1 gm. From the dilute sodium hydroxide washings of the esters, 4 gm. of unchanged acids was recovered and this was esterified in ether solution with diazoethane. The product thus obtained was fractionated and the two fractions were combined with the corresponding fractions obtained from the main esterification.

The first fraction was saponified by refluxing with aqueous-alcoholic potassium hydroxide and the crystalline acid obtained was recrystallized twice from hot water. Alone or in admixture with an authentic specimen of benzoic acid, this acid melted at 124° C.

The ester collected in the second fraction could not be crystallized and it was saponified by refluxing with aqueous-alcoholic potassium hydroxide. It yielded a crystalline acid (20 gm.). This was recrystallized repeatedly from aqueous methanol and from methanol-benzene from which it separated in clusters of prismatic needles, m.p. 147° C. Calc. for $C_{16}H_{16}O_3$: C, 75.00;

H, 6.24%; mol. equiv. 256. Found: C, 75.04, 75.05; H, 6.31, 6.25%; mol. equiv. 252, 253. Some of the acid was dissolved in ether and esterified with diazomethane. The methyl ester was distilled twice and analysed. Calc. for $C_{17}H_{18}O_3$: OCH_3 , 11.48%; mol. wt., 270. Found: OCH_3 , 11.91, 11.93%; mol. wt. (Rast), 260. The Berg test (1) for α -hydroxy-acids was negative. This failure to give the test may possibly be due to the presence of the two phenyl groups in close proximity.

Oxidation of α -Hydroxy- α,γ -diphenylbutyric Acid

It was observed that α -hydroxy- α,γ -diphenylbutyric acid still reduced potassium permanganate. Therefore, the acid (1.0 gm.) was dissolved in purified acetone (50 cc.) and oxidized at room temperature by the addition of finely ground potassium permanganate in portions equivalent to one-quarter atom of oxygen. The first three portions were decolorized very rapidly but the fourth was not completely decolorized after four hours. A little methanol was added to destroy the remaining permanganate and the manganese dioxide filtered and washed with acetone. The combined acetone filtrate and washings were distilled on the steam-bath and the residue was dissolved in ether, washed with dilute sodium hydroxide, and with water. After drying over sodium chloride the ether was distilled off; the residue consisted of an oil that crystallized to a solid mass on cooling. Wt. 0.7 gm. This, after repeated recrystallization from petroleum ether, melted at 72° C. Admixture with β -phenylpropiophenone failed to depress the melting point. The oxime, m.p. 83°, was prepared and found to be identical with β -phenylpropiophenoneoxime.

Isolation of α,γ -Diphenylbutyrolactone

α -Hydroxy- α,γ -diphenylbutyric acid (1.5 gm.) was dissolved in glacial acetic acid (20 cc.) and the solution saturated with hydrogen bromide (action of bromine on tetralin). The solution was then refluxed for three hours, allowed to cool, and poured into cold water (300 cc.). The oil that separated was collected in ether, the solution washed repeatedly with water, and distilled on the steam-bath. The residue was dissolved in aqueous alcohol containing a little sodium hydroxide and the solution shaken in a mechanical shaker for 16 hr. with sodium amalgam. During the reduction the alkalinity was controlled by the occasional addition of acetic acid and the spent amalgam was replaced. After completion of the reduction, the liquor was decanted off and acidified with hydrochloric acid. The precipitated oil was dissolved in ether, washed with water, dried over sodium chloride, and distilled first on the steam-bath to remove the solvent and then *in vacuo*. The product was a yellowish oil, b.p. 195 to 200° C. (2.5 mm.), which crystallized on standing. After six recrystallizations from petroleum ether the melting point was constant at 107°. Calc. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88%. Found: C, 81.05, 81.41; H, 5.67, 5.75%. No depression in melting point was caused by admixture with α,γ -diphenylbutyrolactone prepared by the reduction of β -benzoyl- α -phenylpropionic acid with sodium amalgam.

Synthesis of β -Hydroxy- β,δ -diphenylvaleric Acid

It was believed originally that the styrene degradation acid might be β -hydroxy- β,δ -diphenylvaleric acid, and this was synthesized. The acid is new and although it is not identical with, but a homologue of, the degradation acid, it is thought desirable to put it on record. The ester of the acid was prepared by a Reformatzky reaction from β -phenylpropiofenone (11 gm.) and ethyl bromoacetate (8 gm.) in a mixture of dry benzene (20 cc.) and absolute ether (8 cc.) to which zinc spangles (4 gm.) was added. The product worked up as usual, yielded a crystalline ester which, after crystallization from petroleum ether, melted at 79.5° C. Calc. for $C_{19}H_{22}O_3$: C, 76.50; H, 7.38%. Found: C, 76.62, 76.97; H, 7.61, 7.75%. The ester, when saponified with aqueous-methanolic potassium hydroxide, yielded β -hydroxy- β,δ -diphenylvaleric acid which, after several recrystallizations from methanol-benzene and from hexane, melted at 155° C. Calc. for $C_{17}H_{18}O_3$: C, 75.54; H, 6.67%. Found: C, 75.46, 75.48; H, 6.51, 6.77%.

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THE TERNARY ALLOY SYSTEM: ALUMINIUM-LEAD-SILVER¹

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Abstract

1. The area of partial miscibility for the ternary system, aluminium-lead-silver, has been determined by thermal and chemical analysis. It is found to extend from the binary system aluminium-lead to alloys containing a maximum of 85.58% silver and 4.71% lead by weight.

2. The temperatures of separation of solid phase, bounding this area, have been found to fall at first with addition of silver to the system aluminium-lead, until a temperature of 548.5° C. is reached. This is the temperature of solidification of the alloy that contains silver and aluminium in their eutectic proportions, plus saturation with lead. The temperature then increases to a maximum of about 736° in the alloy containing about 80% silver and 14% lead. This temperature maximum does not coincide with the summit of the mutual solubility curve but lies well to the right of it.

3. No ternary compounds have been found.

4. The ternary eutectic practically coincides with the binary eutectic of the system silver-lead.

5. As far as can be determined by thermal analysis alone, it appears that there is no solid solution of lead in the α , β , or γ phases of the silver-aluminium system.

6. The first peritectic line formed by the addition of lead to the high temperature peritectic point of the silver-aluminium system intersects the partial miscibility curve at 7.90% Al, 7.60% Pb, and 84.50% Ag. The temperature drops from 779.0° to 727.0°.

7. The second peritectic line intersects the partial miscibility curve at 10.30% Al, 4.10% Pb, and 85.60% Ag. The temperature drops from 729.0° to 708.0°.

8. If the partial miscibility curve had not intervened, the two lines would have intersected at 11.00% Al, 15.50% Pb, and 73.50% Ag.

Introduction

Previous Investigations

The binary systems bounding the field of this ternary system are: lead-silver, aluminium-silver, and aluminium-lead. These binary systems are well known and have been worked out in detail so that extensive discussion of them is not necessary here. Bibliographies are given by Hansen (4) and Jänecke (6), but these are incomplete and we therefore subjoin our own, as follows:—

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To save discussion of such well known systems the binary diagrams, drawn from the best available data, are reproduced here for purposes of reference (Figs. 1, 2, and 3).

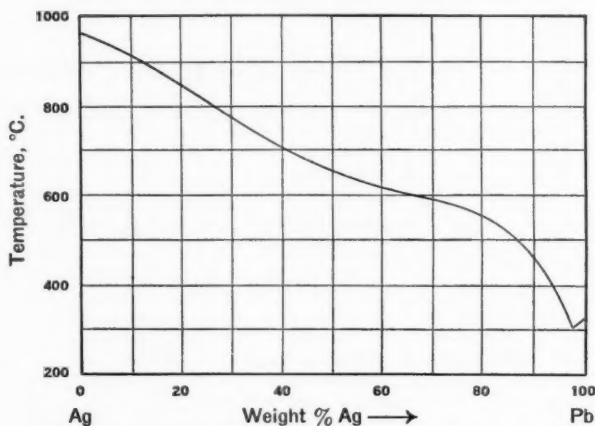


FIG. 1. The system silver-lead (Petrenko).

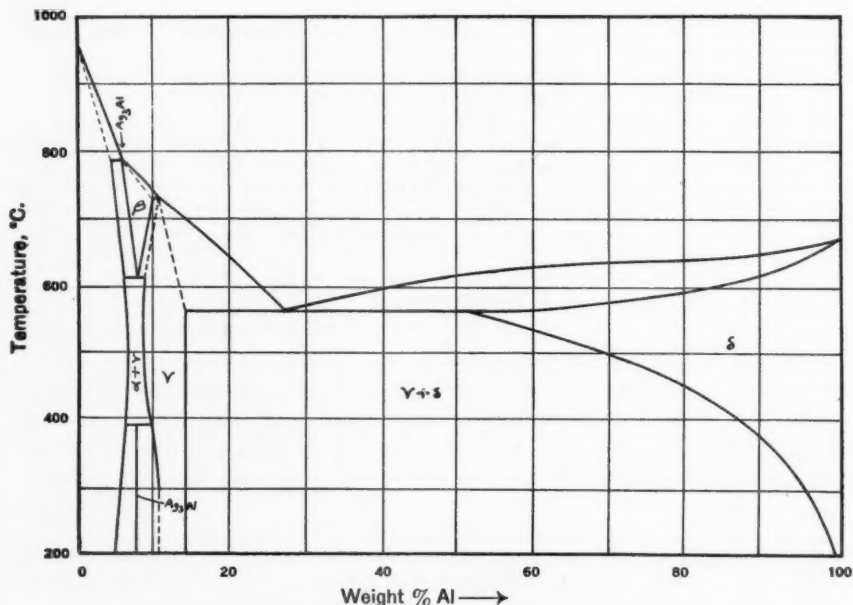


FIG. 2. Composite diagram of the silver-aluminium system.

Coming to the ternary system, we found that little had been done. Wright (16) obtained the critical curve for this system, but no record was made of temperature other than the statement that the alloys were first heated to about 870° C. It is apparent that the partial miscibility of the lead-aluminium system persists over a large area of the ternary diagram.

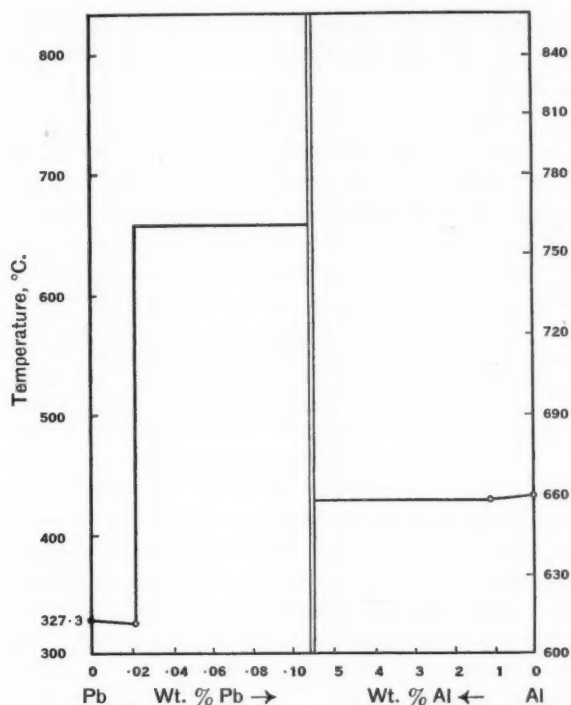


FIG. 3. The system lead-aluminium (Campbell and Ashley).

Lorenz and Erbe (7) studied the ternary system from the point of view of the application of the distribution law. The miscibility curve was plotted for 1000° and for 750° C. They found that at 750°, with a silver content of from 0 to 85% in the lighter phase, and from 0 to 8% in the heavier phase, lead was practically insoluble in aluminium. This conclusion was arrived at, however, on the assumption that all the lead present in the alloys could be explained as colloidal suspension, since it is known that part of it is present in that form. That this is not so has recently been shown by Kempf and van Horn (5) and by Campbell and Ashley (2). In other respects, the results of Lorenz and Erbe are in good agreement with the results of this paper.

Scheme of this Work

The work remaining to be done for completion of the liquidus diagram was:—

1. Redetermination of the miscibility curve for temperatures at which solid phases appear, or, in terms of the solid model, the curve of intersection of the solid of partial miscibility with the planes representing equilibrium of one solid phase with one liquid. In practice this means, the determination,

by thermal analysis, of the temperatures at which liquid alloys separate solid light alloy and solid heavy alloy, followed by chemical analysis of the separated layers.

2. Composition and temperature of the ternary eutectic.

3. The course of the eutectic curve running from the binary eutectic of the silver-aluminium system towards the ternary eutectic.

4. The peritectic lines, running from the two peritectic points of the silver-aluminium system.

In addition to the liquidus diagram, considerable information as to the nature of solid phases was obtained by carrying the thermal analysis down to about 300° C. It is apparent, of course, that for a complete knowledge of the solid phases, investigations by means of the microscope and by X-ray analysis are necessary, but, for these, apparatus was not available. As a matter of practical interest, some measurements of hardness were made.

Experimental

Thermal Analysis

The method employed was principally that of thermal analysis. The technique was standard and requires little explanation. Plato's method (10) of regulated cooling was used; a bank of rheostats was calibrated in equal amounts, so that the introduction of a certain amount of resistance per minute caused the furnace to cool at the rate of 2.5° C. per min. Two platinum-platinrhodium thermocouples were used, one inserted in the melt and the other in a neutral body of copper. The two thermocouples were opposed and connected through a delicate galvanometer, while the thermocouple in the melt was also connected to a potentiometer (method of Roberts-Austen (11)). Sudden displacement of the galvanometer indicated a thermal change at a temperature registered by the potentiometer. An accuracy of $\pm 0.25^\circ$ may be claimed as far as the determination of temperature alone is concerned.

Preparation of Alloys

The lead used had the following impurities: Ag=0.0001%, Cu=0.0025%. The writers are indebted to Dr. Frary and Mr. J. J. Bowman, of the Aluminum Company of America, for some very pure aluminium. This had the following composition:—

Si = 0.007%	Fe = 0.01%	Al = Remainder
Cu = 0.029%	Ti = 0.001%	

The silver used was highest purity fine silver.

Analysis of the Alloys

The alloys produced were occasionally analysed, especially those that had been heated to a high temperature for a length of time, in order to allow for change of composition due to oxidation of aluminium and lead; all the alloys used in the determination of the mutual solubility curve were analysed. Borings were taken from different parts of the alloy and mixed. In some cases

the solid phase is homogeneous, and in none was there evidence of segregation, except, of course, in the region of partial miscibility. In order to ensure homogeneity in the high temperature alloys (outside of the region of partial miscibility) these were quenched in a steel mould.

In the study of the region of partial miscibility, it was found that in alloys rich in aluminium and containing relatively small amounts of silver, the results obtained for the lead analysis were meaningless owing to the fact that aluminium may hold as much as 10% lead in the form of a dispersion. Heat treating these alloys, i.e., allowing them to remain for a long time at a high temperature, greatly reduced the amount of lead present but the results were still not satisfactory. It was finally found necessary to resort to thermal analysis in these cases. For this purpose, an alloy of aluminium and silver of known composition was made up, the temperature of primary crystallization found, and lead then added in quantities of $\frac{1}{2}\%$ at a time. The temperature of primary crystallization was determined each time until a constant temperature was reached. Then, by plotting the temperature of primary crystallization against the percentage of lead added, the true amount of lead in the aluminium layer could be determined. As the percentage of silver in the alloy increased, and therefore the aluminium content decreased, this colloidal effect gradually diminished until, beyond about 80% silver, the phenomenon disappeared entirely and the chemical analysis could be taken as accurate.

The Ternary Eutectic

Since the temperatures in the neighbourhood of this eutectic were comparatively low, a mercurial thermometer was employed to determine the temperature. The thermometer was graduated in 0.5°C . and with the aid of a hand lens could be read to 0.05° . The eutectic alloy was contained in a hard glass test tube, heated electrically.

Enough aluminium was added to lead to saturate it, according to the figures of Campbell and Ashley (2) and thus reach that binary eutectic, and the temperature of solidification taken. Small quantities of silver were now added to the binary eutectic, the temperature of solidification being determined each time. At the attainment of the ternary eutectic an excess of silver was added to prove that the temperature of solidification would go no lower. Before analysis, the alloy was heat treated in the molten state for 24 hr. to allow excess aluminium and silver to separate out by gravity. The alloy was then analysed.

To show that the ternary eutectic is actually a condition of true equilibrium, it should be approached from both sides. Accordingly the binary eutectic, lead-silver, was prepared, and aluminium then added until a constant temperature of solidification was obtained. The alloy was then heat treated and analysed as before.

The Eutectic Curve

This is the curve running from the binary eutectic, silver-aluminium, towards the ternary eutectic point, but limited by its intersection of the area of partial miscibility. It was obtained in the same way as the ternary eutectic, by adding lead to the silver-aluminium binary eutectic until constant temperature was obtained. The higher temperature required the use of the thermocouple apparatus.

The Peritectic Lines

The diagram, outside the area of partial miscibility, was mapped in detail by the method of "sectioning". After each section line had been completed the alloy was analysed chemically and a small correction made for oxidation. Four such sections were studied. The results obtained in each case were plotted on rectangular co-ordinates, a vertical section through the solid model being thus obtained.

Hardness Measurements

These were carried out on most of the alloys prepared, on a standard Brinell hardness testing machine. As the alloys had all been cooled slowly, though not annealed, in the course of the thermal analysis, they are presumably in a more or less stable condition. The quenched alloys might have a different hardness, though the β -phase cannot be preserved by quenching.

Results

THERMAL ANALYSIS

Region of Partial Miscibility

In order to obtain the liquidus curve, 11 alloys of varying composition were prepared, such that the total composition of each alloy lay roughly on the mid-point of a tie-line. In each of these alloys two layers formed, of approximately equal weight. Cooling curves of each alloy were taken, the specimen was then cut vertically and samples were taken from each layer for analysis. The solidification temperatures and the analyses found are given in Table I. The curve obtained from these data is shown in Fig. 4. It should be emphasized that this curve is not strictly a mutual solubility curve, since it is not isothermal, though in fact it is almost so. The curve represents the intersection of an almost vertical sided solid (representing mutual solubility at different temperatures) with the planes of the solid model corresponding to the equilibrium of one liquid with one solid phase.

In Table I, A, the lead content of Alloys 2 to 5 inclusive was determined by means of thermal analysis, as described previously. The high value for lead in Alloy 6 is probably due to the colloidal phenomenon not yet having entirely disappeared. The values for the remaining alloys were obtained by chemical analysis. The figures for Alloy 1, containing no silver, are those of Campbell and Ashley (2).

The Ternary Eutectic

Starting from the aluminium-lead binary eutectic, the temperature of solidification fell, with additions of silver, from 327.0° to 304.1° C. Starting from the silver-lead eutectic and adding aluminium, the temperature remained

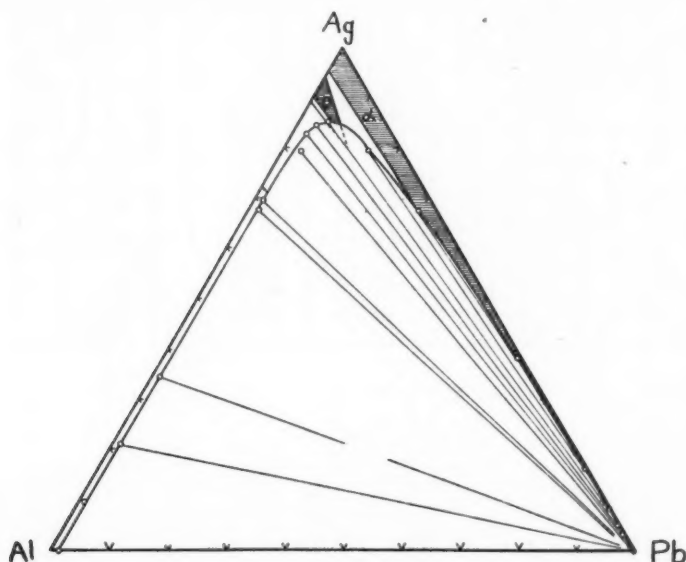


FIG. 4.

TABLE I

ANALYSIS AND TEMPERATURE ARRESTS

A. Lighter alloys					B. Lower alloys				
No. of alloy	Analysis, wt. %			Temp., ° C.	No. of alloy	Analysis, wt. %			Temp., ° C.
	Ag	Al	Pb			Ag	Al	Pb	
1	0.00	98.90	1.10	658.5	1	0.00	0.025	99.975	326.8
2	21.25	77.60	1.15	612.5	2	0.54	0.025	99.40	324.0
3	34.51	64.13	1.36	593.9	3	0.70	0.078	99.18	320.8
4	67.50	30.71	1.73	548.6	4	No data			
5	69.20	29.03	1.73	581.6 (Eutectic 548.7)	5	0.97	0.41	98.62	323.9
6	79.64	17.21	3.11	664.6 (Eutectic 548.1)	6	1.08	0.38	98.54	306.7
7	82.86	14.76	2.38	697.7	7	3.39	0.24	96.37	304.6
8	84.56	12.40	3.04	708.5	8	5.59	0.32	94.09	306.2
9	85.58	9.69	4.71	717.0	9	8.31	0.21	91.48	304.2
10	79.73	5.79	14.48	736.3	10	16.55	0.17	83.33	596.4, 398.9, 304.5
11	67.29	3.38	29.33	726.4	11	38.42	0.30	61.03	304.5

TABLE II
COMPOSITION AND THERMAL EFFECTS IN ALLOYS OF CONSTANT ALUMINIUM/LEAD RATIO

Alloy No.	Wt. % Pb	Wt. % Al	Wt. % Ag	Temperature of thermal effect, °C.	Nature of thermal effect	Comments
SECTION I Al/Pb = 6.8/1						
1	0.70	4.90	94.40	815.2 769.2 (Very weak) 601.8 (Very weak) 396.8 (Very weak)	α -Crystallization First peritectic Eutectoid Compound separation	Fig. 5 (p. 224) shows the plane vertical Section I drawn from these results. The following deductions are made:— The limit of the α -region = 4.90% Al and 0.70% Pb. The first peritectic occurs at a composition of Al = 6.60%, Pb = 1.00%, Ag = 92.40%, and at a temperature of 769.0° C. The second peritectic occurs at a composition of 10.60% Al, 1.50% Pb and 87.90% Ag, at a temperature of 716.0° C. Width of the first peritectic gap = 2.00% (1.70% Al and 0.30% Pb). The maximum width of the β -region = 2.80% (2.40% Al and 0.40% Pb). Width of the second peritectic gap = 1.90% (1.60% Al and 0.30% Pb). The eutectoid temperature remains constant at 601° C. The temperature of compound separation varies from 390 to 410° C.
2	0.80	5.80	93.40	783.6 764.8 597.7 402.7	α -Crystallization First peritectic Eutectoid Compound separation	
3	1.00	6.60	92.40	773.8 763.5 602.5 405.8	β -Crystallization (or peritectic) Eutectoid Compound separation	
4	1.10	7.90	91.00	762.8 612.8 (Very weak) 411.4 (Very weak)	β -Crystallization Eutectoid Compound separation	
5	1.30	9.00	89.70	751.0 718.0 (Very weak)	β -Crystallization Second peritectic	
6	1.40	9.80	88.80	735.0 705.7	β -Crystallization Second peritectic	
7	1.50	10.60	87.90	712.3	Second peritectic	
8	1.60	11.30	87.10	714.5	γ -Crystallization	
9	1.76	12.00	86.24	712.3	γ -Crystallization	
SECTION II Al/Pb = 4.5/1						
1	1.00	3.90	95.10	844.0	α -Crystallization	Fig. 6 (p. 225) shows the plane vertical Section II. The limit of the α -region = 4.06% Al and 1.10% Pb. The first peritectic occurs at a composition of 7.20% Al, 1.60% Pb, 91.20% Ag, and at a temperature of 764.0° C. The second peritectic occurs at a composition of 10.23% Al, 2.27% Pb, and 87.50% Ag, at a temperature of 720.0° C.
2	1.10	4.60	94.30	817.6 763.0 603.0	α -Crystallization First peritectic Eutectoid	
3	1.30	5.20	93.50	793.5 766.7 598.0 401.9	α -Crystallization First peritectic Eutectoid Compound separation	

TABLE II—Continued
COMPOSITION AND THERMAL EFFECTS IN ALLOYS OF CONSTANT ALUMINIUM/LEAD RATIO

Alloy No.	Wt. % Pb	Wt. % Al	Wt. % Ag	Temperature of thermal effect, °C.	Nature of thermal effect	Comments
SECTION II—Continued						
4	1.40	6.00	92.60	780.0 764.0 603.0 404.0	α -Crystallization First peritectic Eutectoid Compound separation	Width of the first peritectic gap = 3.10% (2.60% Al and 0.50% Pb). The maximum width of the β -region = 1.50% (1.20% Al and 0.30% Pb). Width of the second peritectic gap = 2.20% (1.83% Al and 0.37% Pb). The eutectoid temperature remains constant at 601° C. The temperature of compound separation varies from 389° to 406° C.
5	1.60	6.60	91.80	784.7 767.7 601.3 395.4	α -Crystallization First peritectic Eutectoid Compound separation	
6	1.83	7.32	90.85	760.5 598.3 389.0	β -Crystallization Eutectoid Compound separation	
7	1.90	8.40	89.70	760.5 725.0 709.1 599.2 406.2	β -Crystallization Second peritectic Intersects miscibility curve Eutectoid Compound separation	
8	2.00	9.25	88.75	747.7 720.8 705.2 598.0 389.0	β -Crystallization Second peritectic Intersects miscibility curve Eutectoid Compound separation	
9	2.30	9.85	87.85	717.1 704.1	γ -Crystallization Intersects miscibility curve.	
SECTION III Al/Pb = 2.93/1						
1	1.60	4.40	94.00	834.5	α -Crystallization	Fig. 7 (p. 226) shows the plane vertical Section III. The limit of the α -region = 5.20% Al and 1.80% Pb. The first peritectic occurs at a composition of 7.10% Al, 2.40% Pb and 90.50% Ag. at a temperature of 760.0° C. The second peritectic occurs at a composition of 10.40% Al, 3.60% Pb, and 86.00% Ag. at a temperature of 708.0° C. The width of the first peritectic gap = 2.60% (1.86% Al and 0.64% Pb). The maximum width of the β -region = 0.50% (0.37% Al and 0.13% Pb).
2	1.80	5.20	93.00	815.2 774.5 606.7 380.7	α -Crystallization First peritectic Eutectoid Compound separation	
3	2.00	6.00	92.00	768.5 604.5 377.0	First peritectic Eutectoid Compound separation	
4	2.30	6.70	91.00	774.0 761.0 599.0 397.0	α -Crystallization First peritectic Eutectoid Compound separation	

TABLE II—*Concluded*
COMPOSITION AND THERMAL EFFECTS IN ALLOYS OF CONSTANT ALUMINIUM/LEAD RATIO

Alloy No.	Wt. % Pb	Wt. % Al	Wt. % Ag	Temperature of thermal effect, ° C.	Nature of thermal effect	Comments
SECTION III— <i>Concluded</i>						
5	2.60	7.40	90.00	760.0 717.0 (Very weak) 603.0 393.0	β -Crystallization Second peritectic Eutectoid Compound separation	The width of the second peritectic gap = 4.00% (3.00% Al and 1.00% Pb). The eutectoid temperature remains constant at 603° C.
6	2.80	8.20	89.00	751.5 709.5 600.5 (Very weak) 392.5 (Very weak)	β -Crystallization Second peritectic Eutectoid Compound separation	The temperature of compound separation varies from 377° to 397° C.
7	3.10	8.90	88.00	729.0 706.0	β -Crystallization Second peritectic	
8	3.30	9.70	87.00	725.0 707.0	β -Crystallization Second peritectic	
9	3.60	10.40	86.00	708.0	Second peritectic	
SECTION IV Al/Pb = 1.34/1						
1	4.70	6.30	89.00	799.5 750.5 710.3 (Very weak) 595.3 383.0	α -Crystallization First peritectic Intersects miscibility curve Eutectoid Compound separation	Fig. 8 (p. 227) shows the plane vertical Section IV. The first peritectic occurs at a composition of 7.55% Al, 5.59% Pb, and 86.86% Ag, at a temperature of 738.8° C. The second peritectic has disappeared because this section now intersects the area of partial miscibility.
2	5.00	6.70	88.30	777.7 740.7 713.7 (Very weak) 598.3 384.3	α -Crystallization First peritectic Intersects miscibility curve Eutectoid Compound separation	Finally an experiment was carried out with an alloy of the composition 81.00% Ag, 2.00% Al, 17.00% Pb. This showed only α -crystallization occurring at a temperature of 818.0° C., followed by ternary eutectic crystallization at 304.1° C.
3	5.35	7.23	87.42	757.8 740.8 708.1 (Weak) 591.0 380.0	α -Crystallization First peritectic Intersects miscibility curve Eutectoid Compound separation	
4	5.59	7.55	86.86	738.8 711.0 (Weak) 594.2 381.5	First peritectic Intersects miscibility curve Eutectoid Compound separation	

constant at 304.1°. The analyses of both alloys were identical and showed only traces of aluminium, less than 0.1%, with 2.30% silver. In order to improve the sensitivity of the chemical analysis, the aluminium was estimated, in this case, as its compound with 8-hydroxyquinoline. The composition and temperature of the binary eutectic, silver-lead, are given as 2.30% Ag and 300 to 305° by Yoldi and Jiminez (17).

The Eutectic Line

The binary eutectic, silver-aluminium, lies, according to Hansen (3) at 558° C., and contains, according to Petrenko (9), 69% silver. This temperature is lowered to 548.6° by the addition of lead, at a composition of 67.50% Ag, 30.71% Al, 1.73% Pb. Further addition of lead produces no change of temperature, the upper liquid layer being now saturated with lead.

Section Lines

These results are given in somewhat greater detail in Table II because of the importance and intricate nature of the phenomena.

Hardness Measurements

The comparative results of the Brinell hardness tests are given in Table III.

TABLE III

Alloy			Brinell number
Pure lead			4.2
Pure aluminium			15.9
Pure silver			12.7
Binary eutectic, Ag-Al			79.6
Binary eutectic, Ag-Al + 1.73% Pb			66.2
%Ag	%Al	%Pb	
34.51	64.13	1.36	58.3
21.25	77.60	1.15	55.3
79.64	17.21	3.11	63.7
87.50	12.50	—	109.0
94.40	4.90	0.70	124.0
90.85	7.32	1.83	50.3
87.85	9.85	2.30	119.0
91.00	6.70	2.30	116.5
86.00	10.40	3.60	74.0
86.86	7.55	5.59	59.0
81.00	2.00	17.00	17.5
20.00	80.00		50.3

Discussion of Results

Region of Partial Miscibility

In the lighter alloys, the silver content increases until it reaches a maximum of 85.58% (with 4.71% Pb) by weight, after which it falls again. With increasing silver content, the lead content also rises. This increase is very slight at first, rising from 1.10% in the alloy that contains no silver to 1.73%

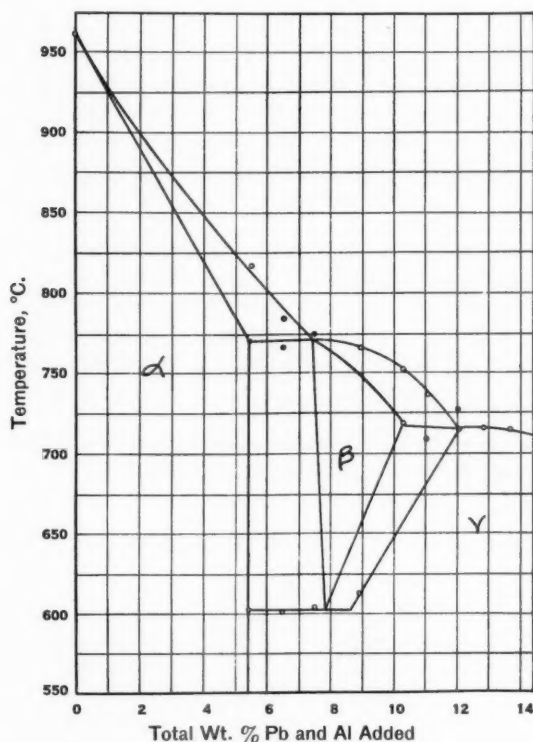


FIG. 5.

in the alloy containing silver and aluminium in the proportions of the binary eutectic of the silver-aluminium system. From this point, the lead content rises very rapidly.

As the amount of silver increases from 0 to 69% by weight, the temperature of solidification of the upper layer falls until it finally reaches a minimum value of 548.5° C. This is the temperature at which the γ -Al eutectic plus 1.73% lead strikes the miscibility curve. Beyond 69% silver, the temperature rises rapidly and continues to rise even in alloys whose composition lies past the summit of the miscibility curve. It finally attains a maximum value of about 736° C. in the alloy containing about 80% silver and 14% lead. Thus the temperature maximum does not coincide with the summit of the miscibility curve.

In the heavier alloys, the silver content rises very slowly until the conjugate lighter alloy has passed to the right of the summit of the curve, after which the content increases very rapidly. The aluminium content remains very small even in alloys with a silver content up to 40%.

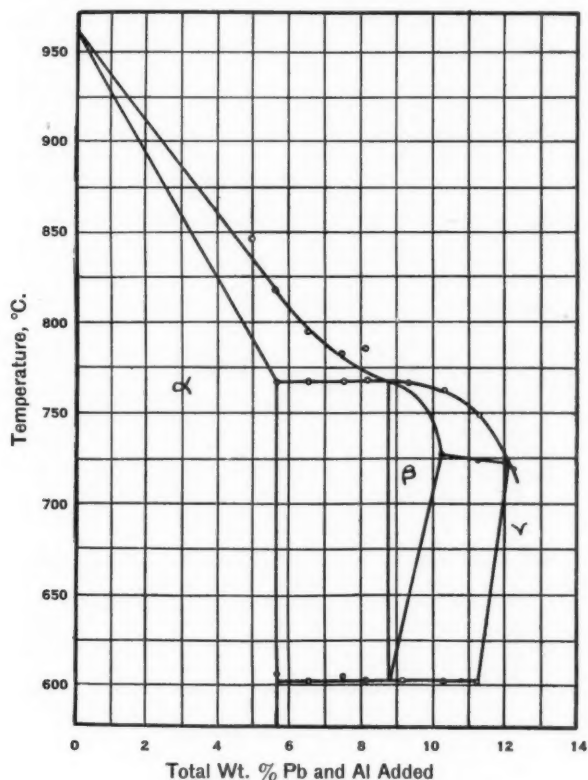


FIG. 6.

With reference to Table I, *B*, it is observed that, in Alloy 10, temperature arrests are observed at temperatures of 596.4° and 398.9° C. These are due to the fact that, in the aluminium-silver system, a β -phase forms owing to a peritectic reaction at 779° C. This phase is, however, stable only above 610° C; below that temperature it decomposes into a mixture of α and γ . This mixture also has a region of limited existence and at a temperature of about 400° C. the β' -phase (AlAg_3) is formed and this is stable at room temperature. Alloy 10 alone shows these transformations because it alone lies in the first peritectic gap. Alloy 9 might be expected to show the second peritectic transformation although it does not, but a very slight error, either in the position of the second peritectic line or in the analysis of Alloy 9, would account for this.

The analyses show that the light alloys always contain more silver than the corresponding heavy alloys and therefore the tie-lines slope uniformly to the right as shown in Fig. 4. To avoid complicating this diagram, the temperatures

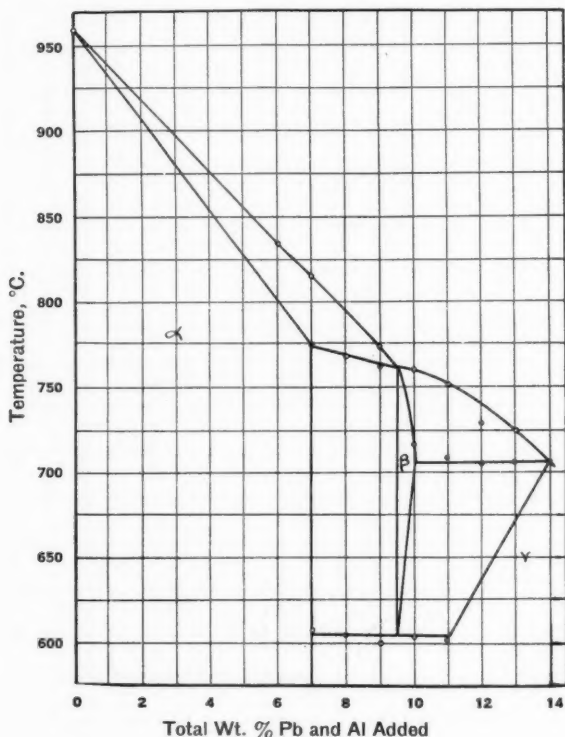


FIG. 7.

of the individual points have not been indicated: these may be found in the table. The diagram is a projection on the base of the solid model, not an isothermal section.

The Ternary Eutectic

The results show that the ternary eutectic point is almost identical with the binary eutectic, silver-lead. The solid phases here are silver, lead and (presumably) γ . The end member of the γ -series of solid solutions is either the compound AgAl_2 , as found by most previous workers, or the compound AlAg_2 , as found by Tishtchenko and Lukash (14).

Solubility of Lead in Solid Phases

Thermal analysis does not show any appreciable solid solubility of lead in the α , β , or γ -phases. The eutectoid reaction $\beta \rightleftharpoons \alpha + \gamma$ would show a temperature change if solid solution of lead in any of these phases occurred, but, as Fig. 9 shows, the variation in eutectoid temperature is that only of experimental error, the temperature varying in different directions, regardless of the amount of lead added.

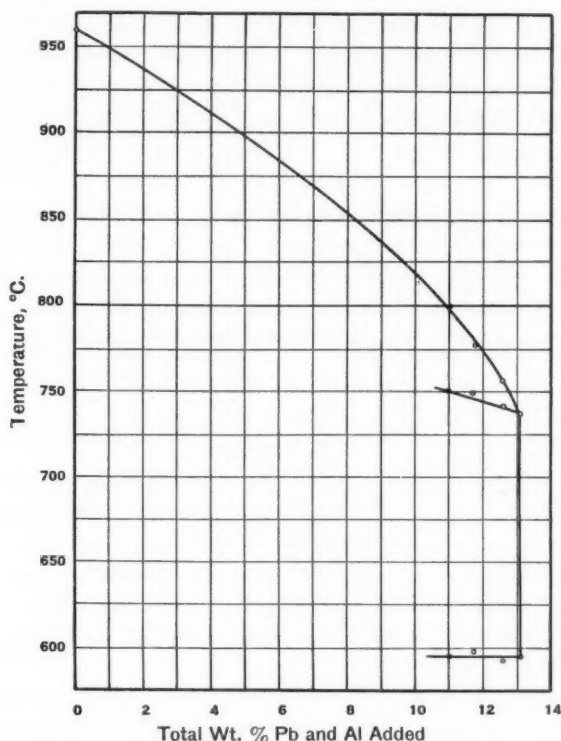


FIG. 8.

The eutectoid temperature has been variously given as 600° (1), 615° (8), 606° (12), and "around 610° C." (15). Our results show an average of 601°.

The temperature of compound separation ($\beta' = \text{Ag}_3\text{Al}$) likewise gives no indication of solid solubility. It was found to vary between 385° and 405° C., regardless of the amount of lead added. This variation is also found in the literature. Different investigators place this temperature at 400° (1), 400° (13), 420° (8), and 456° C. (12).

Investigation of δ -solid solubility proved fruitless since, even with very slow cooling (1° C. per min.), the effect could not be detected in the silver-aluminium system (without lead). This is borne out by Hansen (3), who determined the δ -region micrographically.

We have obtained some direct microscopic evidence of the insolubility of lead in γ -phase. Solubility of lead in α -phase is, a priori, improbable, since the α -phase will possess the silver space lattice, and the lead-silver binary system shows that lead and silver are mutually insoluble in the solid state. Micrographic determination is not possible for the β -region, since according to Obinata and Hagiya (8), Westgren and Bradley (15) and Ageew

and Shoyket (1), the reaction $\beta \rightleftharpoons \alpha + \gamma$ cannot be repressed by quenching. X-ray analysis is necessary to settle the matter conclusively; thermal analysis indicates that lead is insoluble in β -phase.

Fig. 4 is a complete equilibrium diagram, showing all liquidus curves, and areas of solid separation.

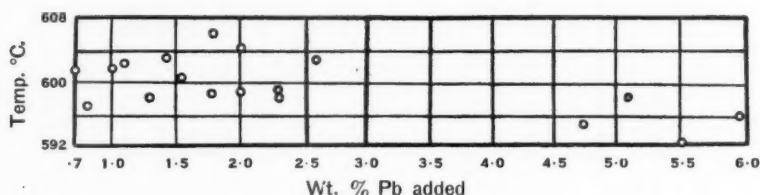


FIG. 9.

Fig. 10 is a magnified section of the silver apex, showing the peritectic lines and the (presumed) areas of solid solubility, together with some isothermal lines.

In the area $ABCK$ primary crystallization of a solid solution of the α -series will take place, whose precise composition will depend on that of the melt. The lead will remain in the residual liquid, which will eventually solidify at the ternary eutectic point.

In the region bounded by the lines BD , BC , DJ and the miscibility curve, heterogeneous solid phases will be produced. A solid solution of the α -series will first separate. When temperature and composition cross the line DJ , interaction of separated α with liquid melt to form β -phase results, but excess α remains unchanged. The residual liquid, which (presumably) contains all the lead, solidifies at the ternary eutectic.

The region of occurrence of homogeneous β is bounded by the area $DJNE$. The β -phase is the primary crystallization. The lead will remain in the residual liquid which will finally solidify at the ternary eutectic.

The area $ENHG$ is also an area of heterogeneity. The primary crystallization is that of β which will change (partially) to γ , when GH is crossed. The residual liquid containing the lead solidifies at the ternary eutectic. The $\beta/(\beta+\gamma)$ boundary EN , is drawn, like that of the $\alpha/(\alpha+\beta)$ boundary BC , by joining the point E (or B) to the opposed angular point, i.e., by assuming that the solid phases are free from lead. The thermal analysis, however, also presents some direct evidence for the position of EN , as reference to the data of the sections will show. Alloys showing eutectoid transformation but no second peritectic should all lie in the area $DJNE$, whereas alloys showing both eutectoid transformation and second peritectic should lie in the area $ENHG$. Owing to supercooling, delayed transition, slowness of solid diffusion, etc., this is not entirely borne out by the experimental data, but it is very

largely. It should be noted that the diagram only represents primary crystallization, in the sense that liquid melt is always present. The diagram does not represent the constitution of the cold alloy because of the impossibility of preserving β by quenching: β always transforms to the pure compound β' on cooling.

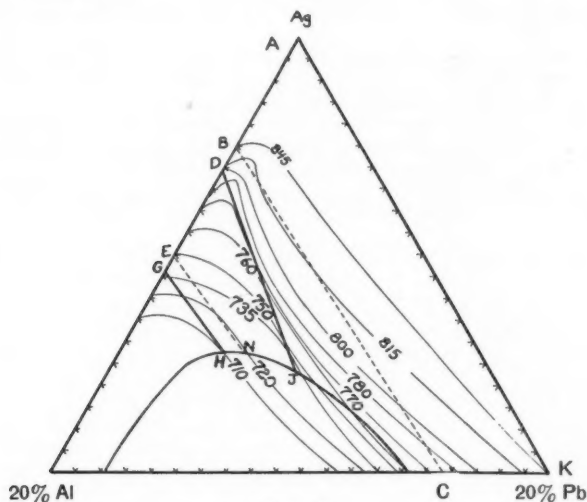


FIG. 10.

The first peritectic line in the silver-aluminium system with increasing addition of lead intersects the partial miscibility curve at 7.90% Al, 7.60% Pb, 84.50% Ag, the temperature dropping from 779° to 727° C. The second peritectic line intersects the partial miscibility curve at 10.30% Al, 4.10% Pb, and 85.60% Ag, the temperature dropping from 729° to 708°. If the partial miscibility curve had not intervened, the two lines would have intersected at 11.00% Al, 15.50% Pb, and 73.50% Ag.

Hardness Measurements

From the table of hardness it is evident that when silver is added to aluminium, the resultant alloy is very much harder than either of the two component metals. When lead is added to the aluminium-silver alloys, its presence reduces this hardness. Although the components are all soft, aluminium being the hardest, the hardness of alloys rich in α , β' , and γ phases approaches that of mild steel. The heterogeneous solids are however much softer.

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